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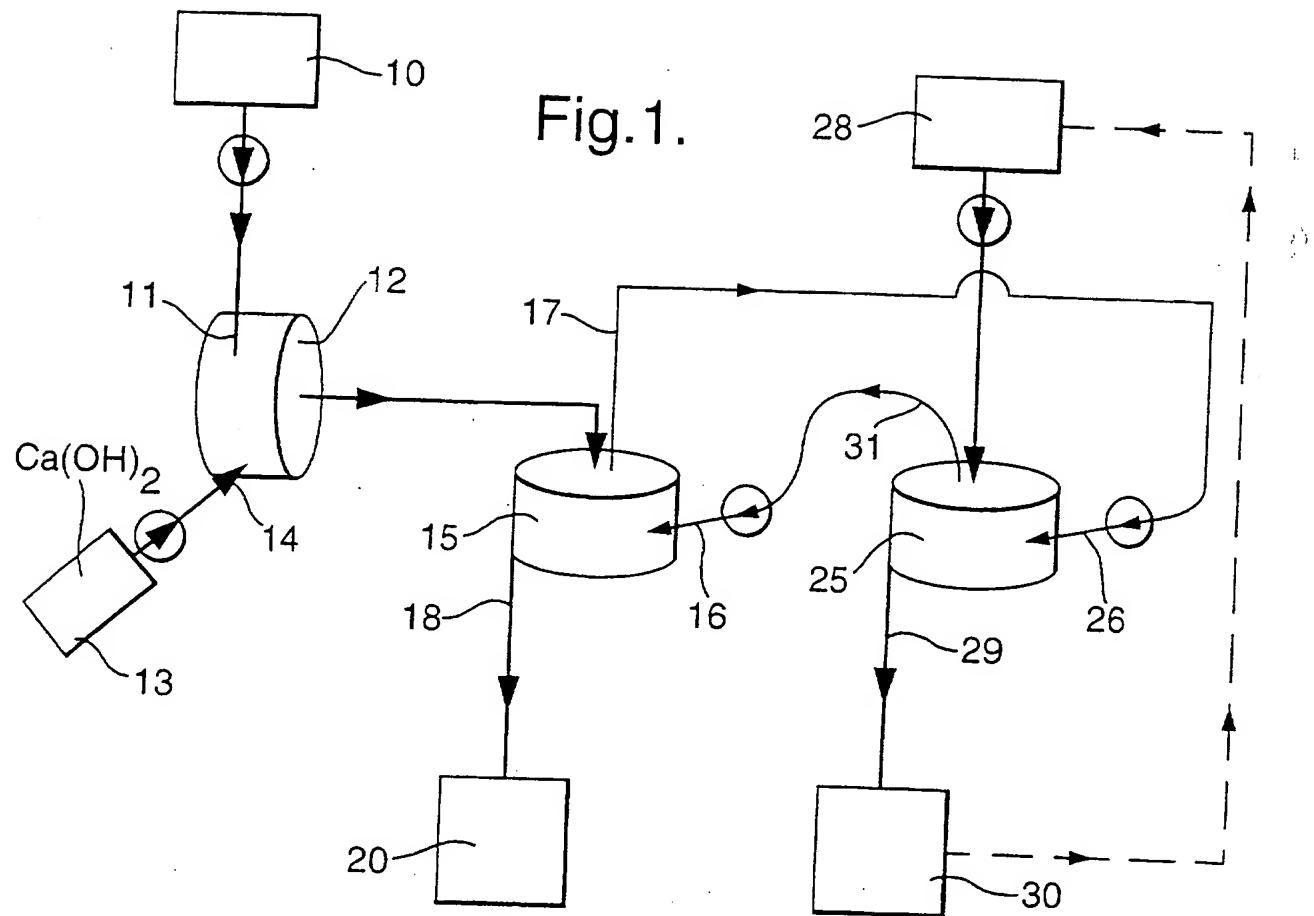


Fig.2.

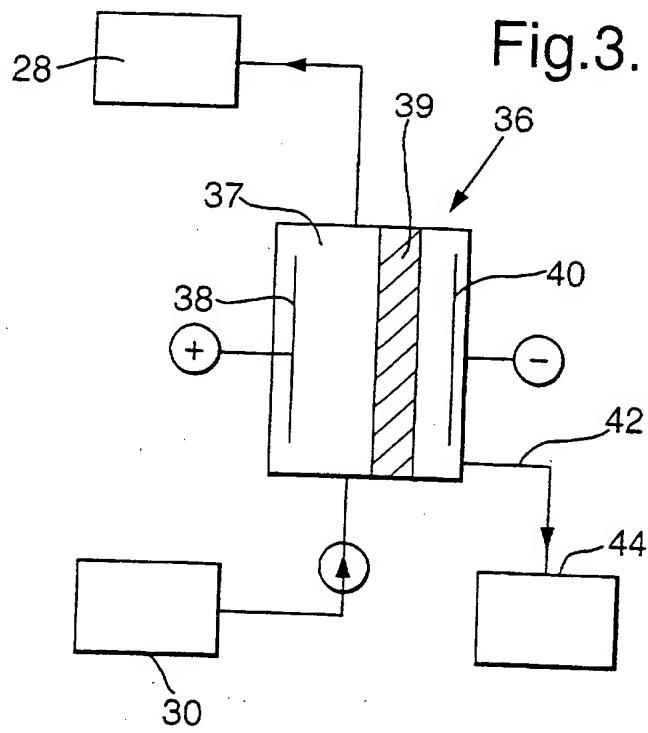
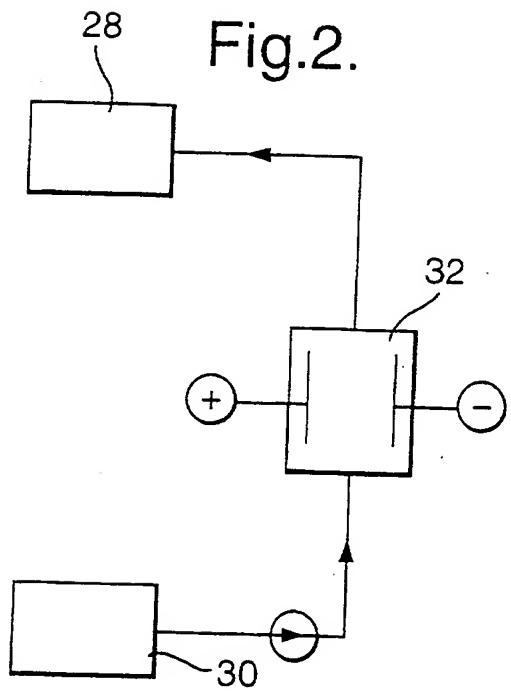


Fig.4.

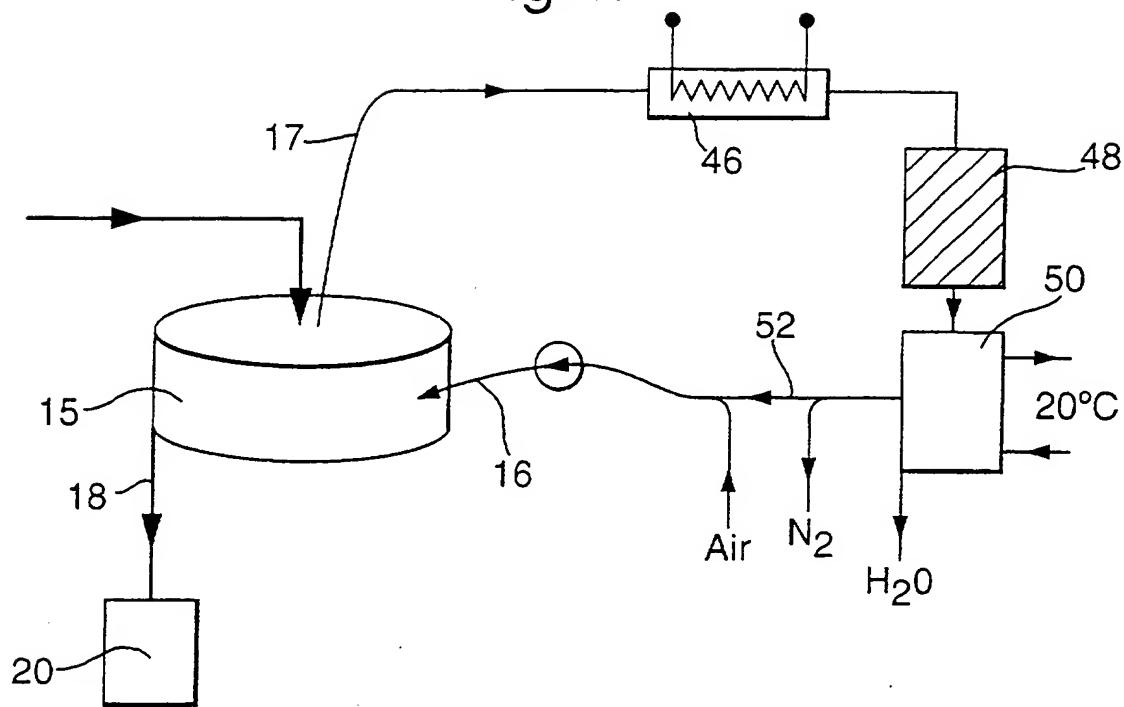
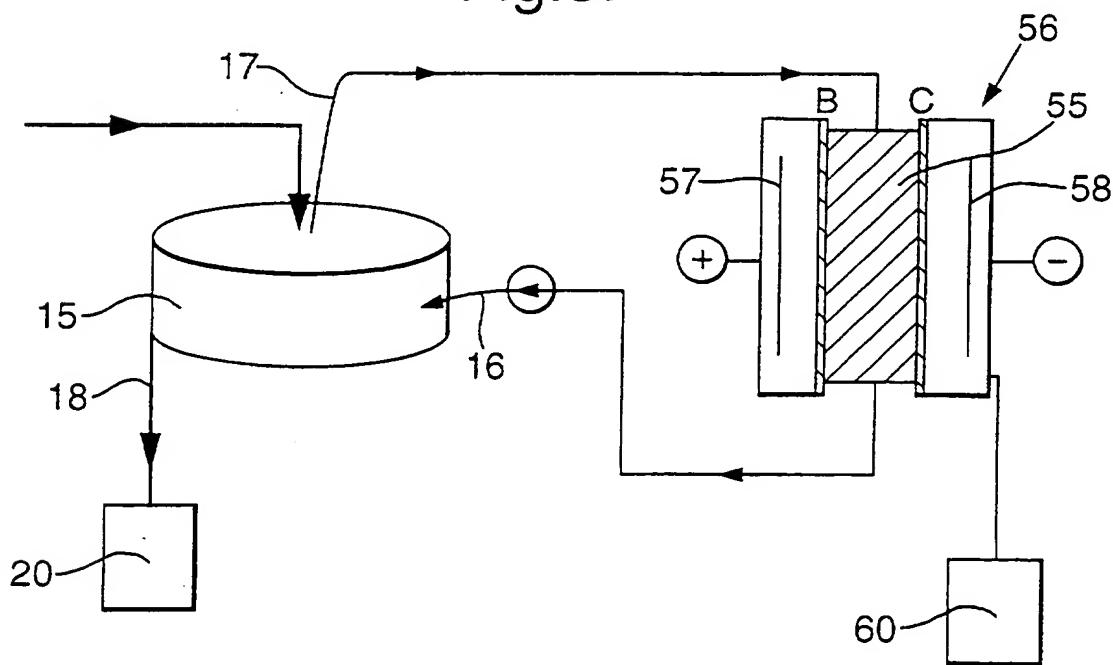


Fig.5.



Ammonia Removal

This invention relates to an apparatus and a method for removing ammonia from a fluid stream.

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To avoid damage to the environment, the discharge of ammonia, or liquids containing ammonia, should be avoided if possible. This applies to the discharge of the the solutions resulting from the regeneration of ion-exchange 10 columns for treatment of boiler feed water, and the effluent from processing sewage sludge, for example. It would therefore be desirable to be able to remove the ammonia from such a solution, either to destroy it, or to convert it into a useful form.

15

A currently accepted method of managing weak ammonia solutions is to steam-strip the solution (after making it alkaline by addition of caustic soda or lime), and then to condense the resulting vapours at about 5°C to produce 20 a solution of substantially pure ammonia at a more useful concentration. Any tail gas will then be scrubbed before venting to the atmosphere. This suffers from the disadvantages of requiring a supply of process steam and means to cool the vapours, and these are not necessarily 25 conveniently available. Packed towers for the stripping operation are prone to fouling, while tray or bubble-towers, which are more resistant to fouling, are more expensive.

30

According to the present invention, in a first aspect, there is provided a process for treating a liquid that may contain ammonia or an ammonium salt, the process comprising the steps of:

35 (a) mixing the liquid with an alkaline material to raise

the pH to above pH 9;

5 (b) stripping ammonia from the mixture by passing the mixture as a spray through a fluidic vortex contactor in counter-current to a gas stream, the gas stream being supplied to a substantially tangential inlet and emerging from an axial outlet, so as to create an ammonia-containing gas stream;

10 (c) treating the gas stream to remove the ammonia either by contact with an ion-exchange material, or by contact with a spray of droplets of a scrubbing liquid; and

15 (d) removing ammonia from the ion-exchange material or from the scrubbing liquid by an electrochemical treatment.

20 Preferably the process also comprises recycling at least part of the treated gas stream for use in the stripping step. This has the benefit that even in the event of failure of the treating step ammonia gas is not released to the environment. Recycling of the gas stream also minimises water evaporation. The gas stream used for stripping the ammonia may be an air stream or a stream of 25 nitrogen.

30 The treatment to remove ammonia may be performed in a variety of different ways. A variety of different scrubbing processes may be utilized. The ammonia-containing gas stream may be scrubbed by contact with an aqueous stream at a neutral or slightly acidic pH. For example if the aqueous stream is dosed with sulphuric acid, the result will be a solution of ammonium sulphate. Alternatively, if the aqueous stream contains sodium 35 chloride or sodium bromide, the resulting solution may be

processed electrochemically so that the ammonia is oxidised to nitrogen gas. The scrubbing may alternatively be performed by passing the gas stream through a porous barrier of cation-exchange material; the 5 ammonium ions trapped by the ion exchange material may be removed by an electric field to produce a concentrated solution of ammonia.

10 The alkaline material used to make the pH rise may be caustic soda (sodium hydroxide) or slaked lime (calcium hydroxide), and the pH is desirably raised to at least pH 9.25. This preferably uses a fluidic vortex mixer to ensure rapid and thorough mixing.

15 A fluidic vortex mixer comprises a vortex chamber with two or more peripheral inlets, at least one of which is substantially tangential, and with an axial outlet. Such a device can achieve very rapid and thorough mixing in a very short space of time; for example the residence 20 time in the mixer may be less than 0.5 s, or even less than 0.1 s, for example 20 ms or 10 ms, though usually at least 1 ms. The chamber is substantially cylindrical, and contains no baffles to disrupt the vortex flow. A fluidic vortex contactor is of a similar structure, a gas 25 flow being fed into a tangential inlet to follow a spiral vortex flow path and to emerge through an axial outlet, while liquid is fed to a spray nozzle at the centre of the chamber, the droplets being sprayed outwardly and emerging as a liquid at the periphery. Again the chamber 30 contains no baffles to disrupt the vortex flow.

The mixture may also be subjected to high-powered ultrasonic irradiation; in the case of slaked lime this can have the effect of dispersing the lime in a high 35 surface area form, so maximizing its utilization. If a

liquid is subjected to an ultrasonic intensity above about 0.3 W/cm^2 , then there is a significant deposition of energy into the liquid through attenuation and non-linear effects. This can be associated with cavitation, 5 in which small bubbles are created which are filled with vapour or gas, and which collapse rapidly during the compression half-cycle of the ultrasonic wave.

Where the scrubbing is performed with an aqueous 10 stream this is preferably performed in counter-current, and also utilises a fluidic vortex contactor.

In a second aspect, the invention provides a process for treating a liquid that may contain ammonia or an 15 ammonium salt, the process comprising the steps of:

(a) mixing the liquid with an alkaline material to raise the pH to above pH 9;

20 (b) stripping ammonia from the mixture by passing the mixture as a spray through a fluidic vortex contactor in counter-current to a gas stream, the gas stream being supplied to a substantially tangential inlet and emerging from an axial outlet, so as to create an ammonia-containing gas stream;

25 (c) treating the gas stream with a catalyst so that the ammonia undergoes catalytic combustion to generate nitrogen and water.

30 In a third aspect, the invention also provides a process for treating a liquid that may contain ammonia or an ammonium salt, the process comprising the steps of:

35 (a) mixing the liquid with an alkaline material to raise

the pH to above pH 9;

(b) stripping ammonia from the mixture by passing the mixture as a spray through a fluidic vortex contactor in 5 counter-current to a stream of steam, the stream being supplied to a substantially tangential inlet and emerging from an axial outlet, so as to create an ammonia-containing vapour stream;

10 (c) condensing the vapour stream by contact with a spray of droplets of a scrubbing liquid in a fluidic vortex contactor, the vapour stream flowing in counter-current to the spray of droplets, and the scrubbing liquid collecting in a sump; and

15 (d) recirculating at least part of the scrubbing liquid from the sump to generate the spray of droplets in the fluidic vortex contactor, and cooling at least the recirculated scrubbing liquid to less than 10°C.

20

The invention also provides apparatus for performing such treatment processes.

25 The invention will now be further and more particularly described, by way of example only, and with reference to the accompanying figures, in which:

30 Figure 1 shows a flow diagram of an apparatus for processing a waste liquid to remove ammonia;

Figure 2 shows diagrammatically an addition to the apparatus of figure 1;

35 Figure 3 shows diagrammatically an alternative addition to the apparatus of figure 1;

Figure 4 shows diagrammatically a modification of the apparatus of figure 1; and

Figure 5 shows diagrammatically an alternative 5 modification to the apparatus of figure 1.

Referring to figure 1, a liquid containing ammonia is stored in a tank 10. The liquid is pumped into a tangential peripheral inlet 11 of a fluidic vortex mixer 12, and a slurry of slaked lime from a tank 13 is pumped through a second tangential peripheral inlet 14 of the fluidic vortex mixer 12 at such a rate that the outflowing mixture is held at pH 12.8. Since the vortex mixer 12 contains no internal baffles it is very unlikely 10 to become fouled by the particulate materials in suspension. The resulting alkaline mixture is passed to a fluidic vortex gas contactor 15, the mixture being sprayed radially outward from the centre of the contactor chamber. Within the contactor chamber 15 the droplets of 15 the mixture travel in counter current to an air stream supplied through a peripheral tangential inlet 16 (and which emerges through an axial outlet 17). The liquid droplets in the vortex chamber 15 hit the wall and a liquid flow consequently emerges from the base through an 20 outlet 18. This outflowing liquid may be stored in a 25 tank 20.

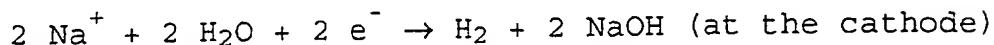
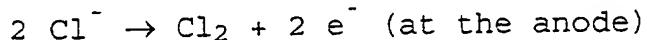
At a temperature of 25°C, the vapour pressure of ammonia increases with the solution pH, up to pH 9.25; as 30 long as the pH is held above that value then the vapour pressure of ammonia is simply related to the solution concentration of ammonia. Consequently as the mixture passes through the gas contactor 15 ammonia evaporates 35 from the droplets and is carried away by the gas emerging through outlet 17. This is an air-stripping process. It

will be appreciated that if the concentration of ammonia remaining in the treated liquid in the tank 20 is still unacceptably high, this liquid may be recycled back to the tank 10 to be subjected to a further air-stripping 5 operation. It will also be appreciated that to maximize the removal of ammonia the pH of the droplets must remain above pH 9.25 until they emerge from the outlet 18, so that the dosing with slaked lime is preferably carried out in accordance with measurements of the pH of the 10 liquid emerging from the outlet 18, maintaining this at say pH 10.

The gas stream emerging from the outlet 17 (and containing ammonia) is then passed through a scrubbing 15 unit comprising a second fluidic vortex gas contactor 25, the gas stream being supplied to a peripheral tangential inlet 26 of this gas contactor 25, and a scrubbing liquid being sprayed radially outward from the centre of the vortex gas contactor 25. This scrubbing liquid is 20 supplied from a tank 28, the droplets impacting with the outer wall of the contactor chamber and emerging through an outlet 29 in the base, to be supplied to a storage tank 30. The air from which ammonia has been scrubbed emerges from an axial outlet 31 and is pumped back to the 25 inlet 16 of the stripping contactor 15. The contactor 25 used for scrubbing is preferably the same size as the gas contactor 15 used for stripping, and they may be stacked on top of each other.

30 In a first example the liquid in the tank 28 comprises sodium chloride (NaCl). As shown in figure 2 (which shows only those features that are additional to those of figure 1) the liquid from the tank 30 is recirculated back to the tank 28 through an 35 electrochemical cell 32, and sodium hydroxide is added to

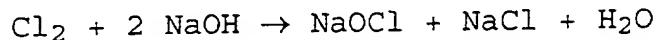
the tank 30 to ensure the pH remains between pH 7 and pH 9. At the anode of the cell 32 at least some of the chloride ions are oxidised to chlorine, while at the cathode water is electrolysed to release hydrogen gas, 5 generating hydroxyl ions. These processes may be represented as:



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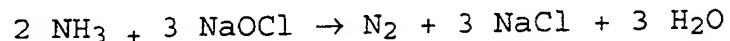
The chlorine thus generated electrochemically reacts with the sodium hydroxide to generate sodium hypochlorite and sodium chloride:

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The sodium hypochlorite then reacts with the ammonia in solution to generate nitrogen gas (and sodium chloride) according to the reaction:

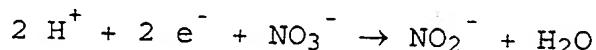
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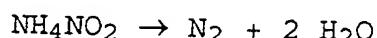
Maintaining the pH between pH 7 and pH 9 ensures that nitrogen trichloride is not generated; suppression of this compound can also be ensured by irradiating the stream exiting the electrochemical cell 32 with ultraviolet radiation. Because the gas stream emerging from the scrubbing unit 25 is recycled back for use in the stripping operation (in the contactor 15), there is 30 no risk of discharge of ammonia gas to the environment. Sodium bromide may be used in place of sodium chloride, and has the benefit that nitrogen tribromide is not formed.

In a second example the liquid in the tank 28 comprises dilute nitric acid. In this case the liquid in the tank 30 is ammonium nitrate. As in figure 2 the liquid from the tank 30 is then pumped through an 5 electrochemical cell 32. The cell 32 has a cathode, for example of lead, at which the nitrate is reduced electrochemically to nitrite:



10

If the liquid is then warmed to above 70°C the ammonium nitrite breaks down to produce nitrogen:



15

In a third example the liquid in the tank 28 is slightly acidic, for example containing dilute sulphuric acid. In this case the liquid in the tank 30 would comprise ammonium sulphate solution. (It will be 20 appreciated that the liquid from the tank 30 may be recirculated back to the tank 28, as indicated by a broken line, in order to absorb more ammonia, and that acid might be added continuously to the tank 28 to maintain an acidic pH.) The liquid collecting in the tank 25 30 may therefore be substantially at pH 7. As shown in figure 3 (which shows only those features which are additional to those of figure 1), this solution of ammonium sulphate is passed through an electrochemical ion exchange cell 36. The cell 36 has a solution 30 compartment 37 through which the solution is passed and then returned to the storage tank 28, and in which is a platinised titanium mesh anode 38. The solution passes between the electrode 38 and a permeable layer 39 formed of an intimate mixture of particulate cation exchange 35 resin and an elastomeric binder, there being a cathode 40

at the rear surface of the layer 39.

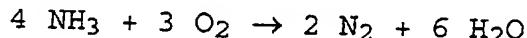
The ammonium ions from the solution are attracted towards the cathode 40 and are absorbed by the ion exchange material of the layer 39. At the anode 38 water is electrolysed, generating hydrogen ions which are attracted towards the cathode 40. The absorbed ammonium ions move, over a period of time, under the influence of the electric field, towards the rear surface of the layer 10 39 (being displaced, to some extent, by hydrogen ions). In addition water from the solution permeates the layer 39; if water permeation were totally unrestricted this would typically provide a flow rate of about 60 litres $m^{-2} h^{-1}$ with a layer 39 of thickness 5 mm. Consequently 15 in the catholyte region behind the layer 39 ammonia solution appears, and this may be bled out through an outlet duct 42 to a storage tank 44. The concentration of ammonium ions in the eluate emerging through this outlet duct 42 can be considerably higher than that of 20 the solution undergoing treatment, and can for example be 0.5 M, this upper limit being set by the possibility of back-diffusion of concentrated solution from the rear of the layer 39 to the front. The resulting ammonia solution in the tank 44 may be a useful product.

25

Alternatively, instead of the cell 36, the solution of ammonium sulphate may be passed through an electrochemical cell (not shown) comprising a flow chamber containing a bed of cation exchange material 30 sandwiched between a cation membrane and a bipolar membrane, these membranes separating the cation exchange material from concentrate chambers, arranged between an anode and a cathode; there may be a stack of such alternating chambers. In a similar way to that in the 35 cell 36, ammonia solution can thereby be generated in the

concentrate chambers.

Referring now to figure 4 there is shown a modification of the apparatus of figure 1 in which the 5 ammonia in the gas stream emerging from the outlet 17 of the stripping vortex contactor 15 is destroyed by combustion. In this example the gas stream is passed through an electrical heater 46 to raise its temperature to 250°C, and then passed through a packed bed 48 of 10 catalyst (containing copper oxide) in which the ammonia reacts with air as follows:



15 (If no catalyst is used, such a combustion will require a higher temperature.) The resulting gas mixture is passed through a condenser 50 to remove the water, and the resulting gas (which is primarily nitrogen) is released to the environment. Fresh air is supplied from the 20 environment to the inlet 16. A duct 52 enables the out-flowing gas from the condenser 50 to be partly recycled to the stripping contactor 15, if desired. It will be appreciated that although the heater 46, catalyst bed 48, and condenser 50 are shown as separate items, they may be 25 combined, for example using a heat exchanger to remove heat from the treated gas while heating the in-flowing gas, and combining the heater with the catalyst bed so the bed is heated directly. The catalyst may be supported within a heat exchanger, this be heated for 30 example by combustion gases rather than relying on electrical heating. It will also be appreciated that this process does not have all the features specified in claim 1.

35 Referring now to figure 5, in another modification

of the apparatus of figure 1 ammonia is again removed from the gas stream emerging from the outlet 17 of the stripping vortex contactor 15 without scrubbing. In this example the gas stream is passed through a packed bed 55 of particulate cation exchange material within an electrodialysis cell 56. Electrodes 57 and 58 in respective electrolytes are provided at each side of the cell 56. The packed bed 55 is between a bipolar membrane B on the side nearest the anode 57 (the bipolar membrane B having its cationic surface adjacent to the packed bed 55), and a cation-selective membrane C on the side nearest the cathode 58. In operation, the damp air stream containing ammonia passes through the packed bed 55, and the ammonia is trapped by the ion exchange material. The voltage applied between the electrodes 57 and 58 is such that water is split into hydrogen and hydroxyl ions within the bipolar membrane B, the hydrogen ions migrating through the packed bed 55 and so displacing the ammonium ions; the ammonium ions hence migrate through the cation-selective membrane C into the electrolyte adjacent to the cathode 58. A concentrated aqueous solution of ammonia therefore forms in the catholyte, and can be bled off into a storage vessel 60.

In some situations, in particular in processing liquid in sewage farms, the liquid may contain both ammonia and urea ($\text{OC}(\text{NH}_2)_2$). The latter slowly breaks down to generate ammonia, but is not removed by the processes described above. In such situations it may therefore be desirable to pretreat the liquid, and this may be done using another fluidic vortex contactor in which the liquid (as a spray of droplets) is contacted with a gas phase containing nitrogen oxide. The nitrogen oxide reacts with the urea to generate nitrogen and carbon dioxide. Suitable nitrogen oxide or oxides may be

generated by electrolysis of nitric acid, so the production rate can be adjusted in accordance with the amount of urea to be treated.

Claims

1. A process for treating a liquid that may contain ammonia or an ammonium salt, the process comprising the
5 steps of:

(a) mixing the liquid with an alkaline material to raise the pH to above pH 9;

10 (b) stripping ammonia from the mixture by passing the mixture as a spray through a fluidic vortex contactor in counter-current to a gas stream, the gas stream being supplied to a substantially tangential inlet and emerging from an axial outlet, so as to create an ammonia-
15 containing gas stream;

(c) treating the gas stream to remove the ammonia either by contact with an ion-exchange material, or by contact with a spray of droplets of a scrubbing liquid; and

20 (d) removing ammonia from the ion-exchange material or from the scrubbing liquid by an electrochemical treatment.

25 2. A process as claimed in claim 1 wherein the gas stream used for stripping the ammonia is of either air or nitrogen.

30 3. A process as claimed in claim 1 or claim 2 wherein the gas stream is treated to remove ammonia by passing it in counter-current to a liquid sprayed as droplets through a fluidic vortex contactor.

35 4. A process as claimed in any one of the preceding claims wherein the ammonia is removed from the ion-

exchange material or from the scrubbing liquid electrochemically so as to generate an aqueous solution of ammonia.

5 5. A process as claimed in any one of claims 1 to 3 wherein the scrubbing liquid is treated electrochemically so that nitrogen is generated from the trapped ammonia.

6. A process as claimed in any one of the preceding 10 claims wherein at least part of the treated gas stream is recycled for use in the stripping step.

7. A process for treating a liquid that may contain ammonia or an ammonium salt, the process comprising the 15 steps of:

(a) mixing the liquid with an alkaline material to raise the pH to above pH 9;

20 (b) stripping ammonia from the mixture by passing the mixture as a spray through a fluidic vortex contactor in counter-current to a gas stream, the gas stream being supplied to a substantially tangential inlet and emerging from an axial outlet, so as to create an ammonia-25 containing gas stream;

(c) treating the gas stream with a catalyst so that the ammonia undergoes catalytic combustion to generate nitrogen and water.

30

8. A process for treating a liquid that may contain ammonia or an ammonium salt, the process comprising the steps of:

35 (a) mixing the liquid with an alkaline material to raise

the pH to above pH 9;

(b) stripping ammonia from the mixture by passing the mixture as a spray through a fluidic vortex contactor in counter-current to a stream of steam, the stream being supplied to a substantially tangential inlet and emerging from an axial outlet, so as to create an ammonia-containing vapour stream;

10 (c) condensing the vapour stream by contact with a spray of droplets of a scrubbing liquid in a fluidic vortex contactor, the vapour stream flowing in counter-current to the spray of droplets, and the scrubbing liquid collecting in a sump; and

15 (d) recirculating at least part of the scrubbing liquid from the sump to generate the spray of droplets in the fluidic vortex contactor, and cooling at least the recirculated scrubbing liquid to less than 10°C.

20 9. A process for treating a liquid substantially as hereinbefore described with reference to, and as shown in, figure 1 and figure 2 or figure 3 or figure 4 or figure 5 of the accompanying drawings.

25 10. An apparatus for treating a liquid as claimed in any one of the preceding claims.

30 15609 MdH

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INVESTOR IN PEOPLE

Application No: GB 0225062.9
Claims searched: 1-6

Examiner: Chris Archer
Date of search: 10 April 2003

Patents Act 1977 : Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
Y	1-6	GB 2014978 A (THAMES WATER) see whole document
Y1-6	1-6	WPI abstract accession no. 1983-775819 [39] & SU 977520 A (UK ZNAK POCHETA NI UGLEKHIMICH) 30.11.1982 (see abstract)
Y1-6	1-6	GB 2104548 A (UNITED TECHNOLOGIES) see whole document

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ONLINE: WPI, EPODOC, JAPIO